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**A Carbon Isotope Mass Balance for an Anoxic Marine Sediment: Isotopic Signatures
of Diagenesis**

ABSTRACT

A carbon isotope mass balance was determined for the sediments of Cape Lookout Bight, NC to constrain the carbon budgets published previously (Martens and Klump, 1984; Martens et al., 1993). The diffusive, ebullitive and burial fluxes of ΣCO_2 and CH_4 , as well as the carbon isotope signatures of these fluxes, were measured. The flux-weighted isotopic signature of the remineralized carbon (-18.9 ± 2.7 per mil) agreed with the isotopic composition of the remineralized organic carbon determined from the particulate organic carbon (POC) $\delta^{13}\text{C}$ profiles (-19.2 ± 0.2), verifying the flux and isotopic signature estimates.

The measured $\delta^{13}\text{C}$ values of the ΣCO_2 and CH_4 diffusive fluxes were significantly different from those calculated from porewater gradients. The differences appear to be influenced by methane oxidation at the sediment-water interface, although other potential processes cannot be excluded.

The isotope mass balance provides important information concerning the locations of potential diagenetic isotope effects. Specifically, the absence of downcore change in the $\delta^{13}\text{C}$ value of the POC fraction and the identical isotopic composition of the POC and the products of remineralization indicate that no isotopic fractionation is expressed during the initial breakdown of the POC, despite its isotopically heterogeneous composition.

INTRODUCTION

Continental shelf and slope sediments are the dominant sites of carbon cycling in marine sediments, comprising only 10% of the seafloor but accounting for approximately 90% of the organic carbon remineralization (Henrichs and Reeburgh, 1987). These environments are thus critical to the global carbon cycle. Carbon remineralization rates in continental margin environments, however, are often difficult to quantify due to the temporal and spatial variability in processes.

Organic carbon reaching the sediments can be remineralized via a succession of oxidative processes requiring oxygen, nitrate, iron, manganese and sulfate as electron acceptors (Mechalas, 1974). After these oxidants are depleted, if sufficient labile organic carbon remains, it may be fermented to CH_4 and CO_2 (Claypool and Kaplan, 1974). A common approach to estimating the rate of organic matter decomposition is the measurement of the sediment water fluxes of the remineralized products, ΣCO_2 and CH_4 and/or the oxidants (Henrichs and Farrington, 1984; Berelson et al., 1987; Mackin and Swider, 1989; McNichol et al., 1991; Reimers et al., 1992; and others).

Significant uncertainties in estimates of sediment-water carbon fluxes are caused by temporal variability in the input of organic matter and associated remineralization rates at individual sites (Martens and Klump, 1984; McNichol et al., 1991; Reimers et al., 1992). One approach to address these uncertainties is to determine a carbon mass balance of the various sources and sinks at individual field sites on time scales appropriate to the site (Martens and Klump, 1984; Berelson et al., 1987; Martens et al., 1993). In temporally variable systems, however, carbon budgets

may not be easily constrained without numerous measurements of fluxes.

An isotope mass balance, accomplished by measurement of the $\delta^{13}\text{C}$ of the individual carbon fluxes and determining the flux-weighted averages of each of the carbon pools, can serve to constrain further the fluxes and rates. Carbon isotope mass balances have been attempted in lake productivity studies (Quay et al., 1986; Herczeg, 1988) and in estuarine studies to quantify seasonal organic matter fluxes to the estuary floor (Lucotte et al., 1991). Alperin (1988) determined an isotope mass balance for the sediments of Skan Bay, Alaska in order to identify the relative rates of degradation of different organic sources. On a global scale, an isotope mass balance of atmospheric methane has been used to estimate source inputs (e.g. Craig et al., 1988; Quay et al., 1991). Most recently, Quay et al. (1992) and Tans et al. (1993) have attempted to use ΣCO_2 $\delta^{13}\text{C}$ measurements of surficial seawater to estimate increases in oceanic uptake. All of these isotope studies have attempted to use a mass balance to estimate a flux or rate that was not easily measured.

Our approach has been to use isotope measurements of all of the major carbon reservoirs and fluxes of the sediments of Cape Lookout Bight, NC, to verify the carbon budget proposed for this site (Martens and Klump, 1984; Martens et al., 1993). Measurement of the isotopic composition of the individual fluxes and reservoirs also allows us to address specific questions about processes at the sediment-water interface such as methane oxidation and to characterize diagenetic isotope effects caused by selective degradation. Cape Lookout was chosen because carbon mass balances for this site have been published previously (Martens and Klump, 1984;

Martens et al., 1993) and remineralization rates vary seasonally in a predictable fashion (Martens et al., 1986).

Remineralization processes (e.g. microbial methane production) can alter the isotopic composition of the individual carbon fluxes, causing a measurable isotope fractionation between the CH_4 and the CO_2 . Diagenetic isotope effects associated with selective remineralization of isotopically distinct organic fractions have also been hypothesized to alter the isotopic signature of the fluxes of the remineralized fraction, and by mass balance, the buried carbon fraction as well (Spiker and Hatcher, 1984; 1987; Alperin, 1988; Fischer, 1989; Benner et al., 1991). In principle, the ^{12}C and ^{13}C mass balance of all identified carbon fluxes (CH_4 , ΣCO_2 , corrected for carbonate dissolution and precipitation) should be the same as the isotopic composition of the remineralized carbon fraction determined from the particulate organic carbon isotope profiles.

FIELD SITE

Cape Lookout Bight (CLB) is a small (1 km^2) back barrier island lagoon with a water depth of 7 meters at the deepest location (Martens and Klump, 1980). All samples were collected at Station A-1, where previous carbon mass balance has been established (Martens and Klump, 1984; Martens et al., 1993). Circulation within the Bight is controlled predominantly by tidal flow (Martens and Klump, 1980; Wells, 1988). The water column above station A-1 remains oxygenated all year (Bartlett, 1981).

Cape Lookout Bight acts as a trap for fine-grained sediments and organic

debris transported seasonally from the Atlantic shelf during storms (Canuel et al., 1990) and from the shallow back barrier lagoons of coastal North Carolina by ebb tidal flows (Martens and Klump, 1980; Chanton et al., 1983). Sediment in Station A-1 accumulates at a rate of 8.4 to 11.8 cm/yr averaged over the upper meter of sediment (Chanton et al., 1983; Canuel et al., 1990). Organic carbon content in the upper meter ranges from approximately 3 to 4 wt. % (Martens and Klump, 1984; Haddad and Martens, 1987; this study) and appears to be derived primarily from phytoplankton and seagrass debris (Haddad and Martens, 1987). Bioirrigation and sediment mixing by animals are not important processes for most of the year at Station A-1 (Bartlett, 1982).

Sulfate reduction is the dominant remineralization process within the upper 10 to 15 cm of the sediment (Martens and Klump, 1984; Crill and Martens, 1987). Methane production occurs below this zone. During summer months (May through October) methane ebullition occurs during low tide conditions when hydrostatic pressure is decreased (Martens and Klump, 1980). Sediment temperatures can vary by more than 20°C through the year and are the driving force behind seasonal changes in rates of microbial processes such as sulfate reduction and methanogenesis (Martens and Klump, 1984).

Based on grain size distributions and annually reproducible pore water nutrient profiles (Klump and Martens, 1981), Martens and Klump, (1984) suggested that "quasi steady state" conditions have existed at Station A-1 at least since the early 1970's. Haddad and Martens (1987) used lignin oxidation product analysis and

isotopic measurements of sediment organic matter as well as degradation rates of metabolizable materials to document yearly steady state input of organic matter on an annual time scale at Station A-1. The agreement in the sedimentation rate determined using ^{210}Pb and ^7Be radiotracers in studies conducted almost 10 years apart (Chanton et al., 1983; Canuel et al., 1990) is further evidence of annual steady state sediment accumulation at Cape Lookout Bight. Laminations seen in sediment cores in the upper 5 cm of winter sediment cores and ^7Be profiles (Canuel et al., 1990) indicate, however, that sedimentation is not uniform on time scales of less than one year. Pore water depth-concentration profiles, fluxes across the sediment-water interface and isotope profiles change rapidly in response to increasing temperature, suggesting that steady state conditions may not be attained on time scales of weeks. Nevertheless, pore water depth integrated and measured rates suggests that the system is near steady state on time scales less than a year.

METHODS

Cores were collected by divers from Station A-1 at 4-8 week intervals from February 1986 through February 1987. Samples also were obtained with a Soutar box core in March, 1986 and 1988. Porewater samples were isolated with a sediment membrane filtration squeezer (Reeburgh, 1967).

ΣCO_2 analyses were performed by injecting one to two ml of porewater into 120 ml evacuated serum bottles capped with crimped, lightly greased rubber stoppers (Alltech #6633). Duplicate or triplicate cores were analyzed. In May, 1986, duplicate samples from the same core as well as samples from a second core were

analyzed. Pore water samples were frozen immediately after collection and maintained frozen until analysis (-18 to -56°C). One ml of 1M phosphoric acid saturated with copper sulfate was added to each porewater sample immediately before analysis. The copper sulfate was added to the sample to precipitate sulfides in order to avoid interference from H₂S. The CO₂ was removed from the bottle by vacuum distillation, purified, and collected cryogenically for isotopic analysis. Sample size was determined manometrically. Bicarbonate and tank CO₂ standards were processed to verify that the procedure was not causing isotopic fractionation and to insure complete gas collection. The precision and accuracy of concentration measurements were 0.4mM and 0.1mM, respectively, based on bicarbonate standards. Reproducibility of the triplicate samples from May, 1986 was 0.5mM.

After purification the CO₂ was collected and sealed in borosilicate tubing and its carbon isotopic composition was measured in one of three laboratories: the Stable Isotope Laboratory, North Carolina State University; NASA-Ames, California; and the Center for Applied Isotope Studies, Athens, Georgia. Interlab comparison among these three labs gave comparable results (± 0.2 per mil, Blair and Carter, 1992). The accuracy and precision of the ΣCO_2 measurements were 0.4 and 0.2 per mil, respectively. Reproducibility from triplicate standard analyses was 0.95 per mil.

Porewater samples were collected on four field dates for analysis of calcium. Following acidification and filtration (0.45 μm), samples for calcium were diluted to 1:20. Samples were analyzed on a Perkin-Elmer 560 Atomic Absorption spectrometer (NCSU - Forestry Department Analytical Laboratory) using a 0.5% Lanthanum

solution. Duplicate analyses had a precision of 0.2mM. A comparison of samples analyzed for Ca^{++} at SUNY-Stony Brook (P. Rude, Marine Sciences) and NCSU agreed to within 0.2mM.

Sediment cores were collected for CH_4 isotopic analysis. Cores were sectioned in 2-3 cm depth intervals and placed in Mason jars containing 10 to 20 ml of 1-3M NaOH. Headspace gas was removed from the Mason jars by syringe through a rubber stopper (Bellco Biotechnology) that had been fitted into the lid. After removing water and CO_2 cryogenically, the methane was converted to CO_2 by passing it through an 790°C furnace packed with CuO using helium as a carrier gas (Matthews and Hayes, 1978). The resultant CO_2 was purified and collected cryogenically. The precision and accuracy of the analyses, based on a methane standard (Scott Specialty Gas), were both 0.3 per mil. Duplicate core samples expressed a maximum difference of 1.6 per mil.

Bubble samples were collected as described in Martens et al. (1986). One ml samples of the bubble gas were removed via syringe from a serum bottle and processed in the same way as the sedimentary methane samples. Tank CH_4 standards, duplicate samples from individual bottles and duplicate and triplicate bottles were analyzed. Precision and accuracy of this procedure are the same as the values given for the sedimentary methane procedure. Reproducibility of samples taken from the same bottle were 0.02 per mil and reproducibility of analyses from individual bottles collected on the same date were 0.2 per mil.

Concentration and isotopic composition measurements of the particulate organic

carbon (POC) were made downcore on sediments collected in August, 1986. Bomb combustion techniques are described in Blair et al. (1987). Precision and accuracy of this procedure, based on NBS-20 standards, are 0.3 and 0.5 per mil, respectively.

Particulate inorganic carbon (PIC) was analyzed on a sediment core collected in May, 1987. The sediment was rinsed with deionized water three times and freeze dried. Ten to 60 mg of sediment was placed in a 120ml serum bottle and sealed with a rubber stopper. The bottle was evacuated and one ml of 0.5M phosphoric acid was injected and allowed to react overnight. Vacuum line collection procedures were the same as for ΣCO_2 porewater samples. Duplicate analyses of the 0-1 cm depth interval gave PIC concentrations within 0.1% and $\delta^{13}\text{C}$ values within 0.01 per mil.

An in situ flux experiment was undertaken in April, 1986. Lucite chambers were placed on the sediment surface and then pushed downward a few cm into the sediment. A battery operated stirring system was used to keep chamber waters mixed. Overlying water samples within the chamber were collected for ΣCO_2 concentration and isotope analyses shortly after emplacement and again at the end of the experiment prior to the next low tide ebullitive event. Cores were taken adjacent to the chambers and analyzed for ΣCO_2 concentration and isotope profiles.

Flux experiments were performed in the laboratory in February 1987 and March 1988. Lucite box core chambers were used to collect an undisturbed section of sediment and overlying water. The chambers were sealed from below and transported in seawater back to the laboratory and placed in a seawater circulation tank to maintain near ambient temperatures. Overlying water samples were taken immediately

after the chambers were stabilized and sampled again twice during the following day. Chambers were circulated at a rate of approximately 15 ml/minute by circulating the overlying water with a peristaltic pump. At the end of the experiment the chambers were subcored and the porewater was extracted for ΣCO_2 concentration and isotopic analyses. During the March, 1988 experiment, overlying water and sediment samples were also collected for CH_4 concentrations and isotopic analyses.

RESULTS

Particulate Organic Carbon

POC content decreases exponentially with values ranging from 4% at the surface to less than 3% at depth (Fig. 2.1a). The $\delta^{13}\text{C}$ values of the POC from this study as well as profiles from Blair et al. (1987) and Blair and Carter (1992) (Fig 2.1b) behave conservatively as a function of depth, indicating that the fraction remineralized must have a $\delta^{13}\text{C}$ value similar to the site average of -19.08 ± 0.26 (Blair and Carter, 1992). More formally, a mass balance calculation can be used to estimate the $\delta^{13}\text{C}$ signal of the remineralized organic carbon:

$$\delta G_0 = \frac{(\%G_{\text{remin}})(\delta G_{\text{remin}}) + (100 - \%G_{\text{remin}})(\delta G_{\text{buried}})}{100} \quad (2)$$

where $\%G_{\text{remin}}$ is the percent of the POC remineralized. Martens and Klump (1984) determined the percent of organic matter remineralized to be $28 \pm 7\%$, based on five POC profiles. The isotopic composition of the POC at the surface (δG_0) is -19.1 ± 0.2 and at depth (δG_{buried}) is -19.2 ± 0.1 (Fig 2.1b). Solving Eqn. (2) for δG_{remin} gives an isotopic signature of the remineralized fraction of the organic matter

of -19.2 ± 0.2 per mil.

ΣCO_2 Diffusive Flux

The results of the ΣCO_2 flux chamber experiments (Table 2.1) were integrated with previous flux measurements (Martens and Klump, 1984) to yield an estimated annual flux of 30.3 ± 4.8 moles- $\text{m}^{-2}\text{-yr}^{-1}$. The error estimate of $\pm 16\%$ is based on the interannual variability of March flux measurements in 1977, 1978 (Martens and Klump, 1984), and 1988 (this study). The ΣCO_2 diffusive flux across the sediment-water interface represents 80% of the remineralized organic carbon that is recycled to the overlying water. This value is consistent with the $84 \pm 18\%$ measured by Martens and Klump (1984). The isotopic signal of the annual diffusive ΣCO_2 flux is estimated to be -15.5 ± 1.2 per mil based on the results of directly measured fluxes (Table 2.1).

Fluxes and isotopic signatures were calculated from pore water gradients for the three flux experiments to compare to the measured flux values (Table 2.1). Calculated fluxes were determined using Fick's 1st Law of diffusion modified for chemical transport in sediments,

$$J_{\text{diffusive}} = -\phi_0 \left(\frac{\partial C}{\partial z} \right)_0 D_s \quad (3)$$

where:

- ϕ_0 = sediment porosity at sediment surface ($0.926 \text{ cm}^3_{\text{pw}}/\text{cm}^3_{\text{wet sed.}}$)
Martens and Klump, 1980)
- D_s = sediment diffusion coefficient (cm^2/sec) (D_0 taken from Li and Gregory (1974) and corrected for sediment tortuosity (Berner 1980))
- $(\partial C/\partial z)_0$ = linear gradient of ΣCO_2 , $\Sigma^{12}\text{CO}_2$ or $\Sigma^{13}\text{CO}_2$ profiles at the sediment water interface (mM/cm)

Calculated and measured fluxes and their isotopic signatures are compared in Table 2.1. The calculated isotopic signal of the March ΣCO_2 flux was also determined by solving for the individual $\Sigma^{12}\text{CO}_2$ and $\Sigma^{13}\text{CO}_2$ concentrations and then calculating the distribution and isotopic signature of each of the following species based on sediment temperature, salinity, pressure and pH: $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, $\text{H}^{12}\text{CO}_3^-$, $\text{H}^{13}\text{CO}_3^-$, $^{12}\text{CO}_3^{=}$, $^{13}\text{CO}_3^{=}$; Deines et al., 1974; Stumm and Morgan, 1981) (Table 2.2; See appendix for description). pH data were taken from Chanton (1985). Individual gradients for each of these species were calculated and the corresponding diffusion coefficients were used in Eqn. 3 (Unver and Himmelblau, 1964; Li and Gregory, 1974; Friedman and O'Neil, 1977; O'Leary, 1984). The resulting isotopic signal of ΣCO_2 flux was compared to a flux based only on the gradients of $\Sigma^{12}\text{CO}_2$ and $\Sigma^{13}\text{CO}_2$ (Table 2.2). The individual species were calculated because previous studies had found significant diffusion of $\text{CO}_3^{=}$ into the sediment despite the net flux of ΣCO_2 out of the sediment (Sayles and Curry, 1988; McNichol et al., 1991). There was no difference in the calculated isotope signal of the ΣCO_2 flux using either approach and so individual species gradient calculations were not applied to the February and April fluxes. Application of a range of pH values (6-8) for the 0-1 cm interval shifted the resulting isotopic signal by less than 1 per mil.

The isotope signature of the calculated ΣCO_2 flux was consistently 6 to 7 per mil enriched in ^{13}C compared to the measured values (Table 2.1). The measured fluxes were slightly larger than the calculated fluxes except in the April *in situ* experiment in which the flux was calculated using porewater gradients from a core

near the chamber.

Burial of ΣCO_2

Burial of ΣCO_2 accounts for a flux of 6.6 ± 0.5 moles- m^{-2} - yr^{-1} with an isotopic signature of $+8.3 \pm 1.5$ per mil. The burial flux was determined using an average of ΣCO_2 concentrations measured at depths between 35 and 40 cm depth (Fig. 2.2) and applying the following equation:

$$J_{\text{burial}} = C_{\infty} \omega_{\infty} \phi_{\infty} \quad (4)$$

where

ϕ_{∞} = sediment porosity at depth ($0.85 \text{ cm}^3_{\text{pw}}/\text{cm}^3_{\text{wet sed.}}$; Chanton, 1985)
 ω_{∞} = sediment accumulation rate at depth (10 cm/yr; Chanton et al., 1983),
 C_{∞} = average concentration of ΣCO_2 at 35 to 40cm (mM/cm).

The burial depth of 40 cm was chosen because the ΣCO_2 concentration profiles are nearly asymptotic and greater than 95% of the remineralization occurs above this horizon (Martens and Klump, 1984). The isotopic signal of the buried ΣCO_2 of $+8.3 \pm 1.5$ per mil was determined by averaging the isotopic values measured at depths of 35 to 40 cm.

CH_4 Bubble Flux

Methane ebullitive fluxes were measured previously (Martens and Chanton, 1989; Martens et al., 1986). The annual ebullitive flux is calculated to be 6.4 ± 0.8 moles- m^{-2} - yr^{-1} based on fluxes measured from 1976 to 1986 (Table 2.3). The isotopic signature of the ebullitive flux of -60.0 ± 1.2 is based on flux-weighted average monthly methane measurements (Martens et al., 1986; Fig. 2.3). The isotope

measurements (Fig. 2.3) show strong seasonality, with relatively ^{13}C -enriched methane consistently released during the period of peak production (July-August).

CO_2 Bubble Flux

Ebullition strips a portion of the dissolved CO_2 from the porewater. The CO_2 ebullitive flux, $0.13 \pm 0.05 \text{ moles-m}^{-2}\text{-yr}^{-1}$ has an annual $\delta^{13}\text{C}$ value of -8.5 ± 1.4 per mil (Martens et al., 1986). The more negative CO_2 $\delta^{13}\text{C}$ values were measured in the summer months corresponding to the period of highest remineralization rates and the most depleted ΣCO_2 values measured in the sediment (Fig. 2.2; Martens et al., 1986).

CH_4 Diffusive Flux

The annual methane diffusive flux of $0.85 \pm 0.8 \text{ moles-m}^{-2}\text{-yr}^{-1}$ was taken from Martens and Klump (1980) and is based on pore water methane profiles and saturation calculations. The measured isotope signature of the methane flux is estimated to be -50.5 ± 0.3 per mil, based on the two flux chamber measurements from this study. The diffusive signal is 9.5 per mil enriched in ^{13}C relative to the annual methane ebullient isotope signal (Martens et al., 1986; this study) and is 4 per mil enriched compared to the diffusive flux calculated from pore water gradients of methane for March (-54.0 ± 0.3 per mil; Table 2.1).

No attempt to determine the seasonality of this signature was made, however, a sensitivity of this flux to the overall isotopic signature of the remineralized fraction was performed. Assuming that either all or none of the diffusive flux was oxidized (the probable cause for the isotopic signature that is different from the methane

produced in the sediment) resulted in less than a 0.5 per mil shift in the isotopic signature of the remineralized carbon.

CH₄ Burial Flux

The burial rate of methane has been calculated to be 0.14 ± 0.02 moles-m⁻²-yr⁻¹ (Martens et al., 1993). The $\delta^{13}\text{C}$ value of the buried CH₄ (-59.9 ± 1.9) was determined by averaging the isotopic signal of the sedimentary methane at 40 cm (Fig. 2.4). This signal is not significantly different than the methane bubble flux value of -60.0 ± 1.2 per mil, indicating that the ebullitive and burial processes are not influenced by oxidation or transport isotope effects (Martens et al., 1986; Chanton and Dacey, 1991).

Solid Phase Inorganic Carbon

Ca⁺⁺ concentration profiles increase from overlying water values in the upper few centimeters and then decrease with depth (Fig. 2.5a). The rates of dissolution and precipitation of particulate inorganic carbon (PIC) were estimated from these porewater Ca⁺⁺ profiles by assuming that an increase in the Ca⁺⁺ concentration profile was caused by dissolution and a decrease in concentration was caused by precipitation of PIC. The Ca⁺⁺ porewater linear concentration gradients were used in the 0-5 and 5-25 cm intervals to estimate the dissolution and precipitation rate of CaCO₃ respectively. The bulk sediment diffusivity for Ca⁺⁺ (D_s) was determined by correcting the diffusion coefficients for Ca⁺⁺ measured in seawater (Li and Gregory, 1974) for the given temperature and sediment tortuosity (Berner, 1980).

The isotopic composition of the PIC that was assumed to have dissolved in the

0-5cm depth interval was determined by averaging the measured isotopic composition of the PIC within the dissolution zone (Fig. 2.5b). The isotopic composition of the assumed precipitated carbonate of -3.8 ± 3.8 per mil is based on the average isotopic value of the DIC pool in the 5-25 cm depth interval from the same months as the measured Ca^{++} profiles (see Fig. 2.2). The use of the Ca^{++} profiles to determine the PIC flux implies that CaCO_3 is the dominant species involved in the dissolution and precipitation processes. To a first approximation, this appears to be true since Mg^{++} concentration profiles showed no significant trends and Sr^{++} concentrations, which mimicked the Ca^{++} profiles, were an order of magnitude lower in concentration than the Ca^{++} values (see Appendices for Mg^{++} and Sr^{++} results). The decrease in Ca^{++} concentration at depth may be a result of precipitation after core recovery because of the oversaturated nature of the porewaters, thus the calculated precipitation rate should be regarded as an upper limit.

The Carbon Isotope Mass Balance

The carbon isotope mass balance determined as described above is summarized in Table 2.4 and shown schematically in Fig. 2.6. The total flux (J_{total}) is defined as the sum of the buried, bubble and diffusive fluxes of ΣCO_2 and CH_4 . To determine the isotopic composition of the portion of J_{total} that results directly from remineralization of the POC (J_{remin}), the contributions of carbonate dissolution and precipitation need to be accounted for:

$$J_{\text{total}} = J_{\text{remin}} + J_{\text{diss}} + J_{\text{precip}} \quad (5)$$

$$(J_{total}) (\delta_{total}) = (J_{remin}) (\delta_{remin}) + (J_{diss}) (\delta_{diss}) + (J_{precip}) (\delta_{precip}) \quad (6)$$

Using eqns. 5 and 6, the isotopic composition of the remineralized carbon is estimated to be -18.9 ± 2.7 per mil, which is in excellent agreement with the remineralized organic matter signal determined from the POC profiles (-19.2 ± 0.2 per mil).

The error associated with the estimated signature of the remineralized carbon pool of 2.7 per mil is primarily due to interannual variability in fluxes and the errors associated with the isotopic composition of the diffusive ΣCO_2 flux. The annual ΣCO_2 flux makes up approximately 70% of the remineralized carbon fraction, and therefore, the budget is very sensitive to the isotopic value assigned to this flux. The internal consistency of the mass balance suggests that despite the small data sets used to determine the methane and ΣCO_2 diffusive fluxes and the interannual variability, the values are realistic estimates of the isotopic signature of these fluxes.

The isotopic composition of the diffusive CH_4 flux was calculated from a single experiment conducted in March. There is undoubtedly some seasonality to this signal that is not included in the estimate used here, but as noted, the small size of this flux precludes it from strongly affecting the overall isotopic signature of the remineralized carbon.

The isotopic composition of the dissolved organic carbon (DOC) flux has not been measured and consequently is not included in this budget. The diffusive and burial DOC fluxes should not significantly influence the overall isotope mass balance

because they represent only 5% of the remineralized carbon flux (Martens et al., 1993), and the isotopic composition of DOC fractions in similar environments are typically within 2-3 per mil of the particulate organic carbon pool (Williams and Gordon, 1970; Nissenbaum et al., 1972; Brown et al., 1972; Orem et al., 1986; Alperin, 1988).

DISCUSSION

The successful isotopic mass balance of the isotopic signature of the sources and sinks of carbon verifies the carbon budget determined for Cape Lookout as well as the isotopic signatures of the different carbon fluxes at a site that experiences significant seasonal variations. More importantly, the isotope mass balance allows us to constrain further our interpretations of certain processes occurring in this system to a degree previously not possible. These processes are discussed below in the context of the balanced carbon isotope budget.

Surficial processes influencing ΣCO_2 and CH_4 fluxes

The diffusive fluxes of both ΣCO_2 and CH_4 and their associated isotopic signatures were directly measured in chamber experiments. Pore water analyses of the flux chamber sediments were made so that the fluxes and their isotopic signature could be estimated from the concentration gradients at the sediment-water interface using Fick's 1st Law (Eqn. 3). Our original intent was to use the monthly ΣCO_2 profiles (Fig. 2.2) to determine the annual $\delta^{13}\text{C}$ value of the diffusive flux. The comparison of measured and calculated ΣCO_2 fluxes and their associated isotopic signatures revealed that the calculated isotopic compositions of the fluxes were consistently 6-7

per mil enriched in ^{13}C relative to the measured values (Table 2.1). The calculated diffusive flux of CH_4 was greater and depleted in ^{13}C relative to the measured CH_4 flux (Table 2.1). Several possible mechanisms that could account for the discrepancies between the calculated and measured isotopic signatures of these fluxes are discussed below.

In theory, differential diffusion of the inorganic carbon species, CO_2 , HCO_3^- , and $\text{CO}_3^{=}$, because of pH gradients across the sediment-water interface, could influence the isotopic composition of the flux of ΣCO_2 and the sedimentary ΣCO_2 pool. The apparent production of ΣCO_2 that is significantly enriched in ^{13}C relative to the organic carbon has been noted in coastal and deep-sea sediments and has been interpreted to result from the diffusion of ^{13}C -depleted CO_2 out of and relatively ^{13}C -enriched $\text{CO}_3^{=}$ into the sediment (McNichol, 1986; Sayles and Curry, 1988; McNichol et al., 1991). Calculations of the individual fluxes and isotopic signals of CO_2 , HCO_3^- and $\text{CO}_3^{=}$ from the March flux experiment demonstrate that the magnitude of the $\text{CO}_3^{=}$ flux is insufficient to alter significantly the overall isotopic ΣCO_2 signal and thus this mechanism can be ruled out for Cape Lookout sediments (Table 2.2).

Differences in the diffusion coefficient of isotopically substituted species would, if they exist, contribute to apparent diffusion isotope effects. For example, the ratio of the diffusion coefficient for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in water ($^{12}\text{D}/^{13}\text{D}$) is 1.0007 ± 0.0002 at 25°C (O'Leary, 1984). This fractionation has been included in the calculations of the ΣCO_2 isotopic signal (Table 2.1). To our knowledge, the potential

isotope effects associated with the diffusion of HCO_3^- , $\text{CO}_3^{=}$ or CH_4 have not been measured.

We consider methane oxidation in surficial sediments to be a source of ^{13}C -depleted material to the diffusive ΣCO_2 flux. Methane oxidation could also explain the discrepancies in the measured and calculated CH_4 fluxes. Evidence for CH_4 oxidation includes $^{14}\text{CH}_4$ -tracer studies (M. Alperin, pers. comm.), and the ^{12}C -depleted CH_4 in the winter surface sediments at Station A-1 (Fig. 2.4). Methane oxidizing bacteria preferentially utilize $^{12}\text{CH}_4$ (Silverman and Oyama, 1968; Barker and Fritz, 1981; Coleman et al., 1981; Whiticar and Faber, 1986; King et al., 1989). The fractionation factor ($^{12}\text{k}/^{13}\text{k}$) for aerobic oxidation of CH_4 ranges from 1.005 to 1.031 in culture (See Table 1 in Whiticar and Faber, 1986). An estimate of the fractionation factor for methane oxidation in the surficial sediments of CLB can be determined if it is assumed that the difference between the measured and calculated methane isotope signal of the March flux experiment is entirely the result of methane oxidation:

$$\delta_{\text{calc}} = (\delta_{\text{meas}} (1 - F_{\text{ox}})) + (\delta_{\text{ox}} F_{\text{ox}}) \quad (7)$$

where F_{ox} is the fraction of the potential diffusive flux of methane that has been oxidized, and δ_{calc} and δ_{meas} are the isotopic compositions of the calculated and measured fluxes (-54.0 ± 0.3 and -50.5 ± 0.3 , respectively) (Table 2.1). F_{ox} was estimated to be 0.32 using the equation:

Accordingly, δ_{ox} is -61.5 per mil and the fractionation factor (α) can be estimated using the following relationship:

$$F_{ox} = 1 - \left(\frac{J_{meas}}{J_{calc}} \right) \quad (8)$$

$$\alpha = \frac{(\delta_{meas} + 10^3)}{(\delta_{ox} + 10^3)} \quad (9)$$

The calculated α is 1.012 ± 0.005 , which falls within the range of both the culture studies mentioned above, and the range determined by Whiticar and Faber (1986) for methane oxidation in natural systems ($\alpha = 1.002$ to 1.014).

If it is assumed that the difference between measured and calculated CH_4 fluxes is due to CH_4 oxidation alone, then only $14 \mu\text{moles}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ of CO_2 are added to the ΣCO_2 flux with an isotopic signal of -61.5 per mil (Table 2.1). This small addition of ^{13}C -depleted CO_2 shifts the calculated ΣCO_2 flux by less than one per mil, and thus does not fully explain the discrepancy between the measured and calculated isotopic values of the ΣCO_2 flux.

Diagenetic Isotope Effects

The carbon isotope mass balance allows us to address the effects of early diagenesis on the isotopic composition of the organic matter that is deposited at Cape Lookout Bight. For the purposes of this discussion, a diagenetic isotope effect is defined as any process that alters the isotopic composition of the organic carbon or creates isotopically distinct pools of carbon after the original organic matter is deposited in a sediment. Selective degradation of isotopically heterogeneous fractions, or kinetic isotope effects associated with various diagenetic processes could result in a

diagenetic isotope effect. The well known isotopic discrimination associated with biogenic methane formation is included in this definition.

In principle, Cape Lookout Bight is an ideal location to investigate potential isotopic effects because of its nearly steady state annual input of organic matter. In addition, Cape Lookout Bight receives organic matter from a variety of isotopically distinct sources such as phytoplankton and seagrasses, as indicated by isotopic measurements, lignin and lipid analyses (Haddad, 1989; Blair and Carter, 1992). Isotopic differences apparently exist between compound classes at this site as well, as indicated by the average $\delta^{13}\text{C}$ values of fatty acids (-22.1 ± 0.5), neutral lipids (-22.9 ± 0.3) and POC (-19.08 ± 0.26) fractions (Blair and Carter, 1992). Thus, given that nearly 30% of the organic matter delivered to site A-1 is remineralized, a diagenetic isotope effect might be expected, if any of these organic fractions were selectively degraded. Surprisingly, the downcore profiles of the POC $\delta^{13}\text{C}$ values and the isotope mass balance of the ΣCO_2 and CH_4 fluxes provide no evidence for selective degradation or preservation of isotopically distinct organic pools. McArthur (1989), Cronin and Morris (1982), Reimers and Suess (1983) and others, also found no indication of an isotopic diagenetic effect in the organic carbon record from a variety of sediment types and ages. This is in contrast to observations made in marine sediments of Skan Bay (Alperin, 1988) where changes in the isotopic composition of the organic matter downcore could be attributed to different rates of remineralization of the dominant organic matter sources, and Mangrove Lake, Bermuda where a ^{12}C enrichment downcore in the sediments was attributed to selective preservation (Spiker

and Hatcher, 1984).

The absence of any expressed isotope effect associated with the input and early diagenesis of organic matter at CLB is surprising since the inputs are isotopically distinct. The analyses of both the deposited and buried fractions of the organic matter of Haddad (1989) and Martens et al. (1993) indicated that the organic matter that was remineralized was most similar to an algal/bacterial source based on the C/N ratios and the loss of biochemical components downcore. The carbon isotope mass balance can be explained most simply by a remineralized fraction that is a mixture of two sources, predominantly algal/bacterial and a vascular plant component.

The large isotopic difference observed between the POC and CH₄ indicates that isotope fractionation occurs during some step or steps in the production of methane from the breakdown of organic matter. Large isotope effects are associated with the reduction of CO₂ and the dissimilation of acetate to form CH₄ at this site (Blair and Carter, 1992; Blair et al., 1993). The carbon isotope budget should allow us to determine if CO₂ reduction and acetate dissimilation are masking other diagenetic isotope effects occurring during the initial breakdown of organic matter at Cape Lookout.

The carbon isotope mass balance, when considered in light of the downcore $\delta^{13}\text{C}$ acetate measurements of Blair and Carter (1992) indicate that there is little or no fractionation in the breakdown of high molecular weight compounds (biopolymers) to form the low molecular weight biomonomers. If there was isotopic fractionation in the initial breakdown of the organic matter, one would expect to see $\delta^{13}\text{C}$ acetate

measurements in the sulfate zone that were very different from the $\delta^{13}\text{C}$ POC measurements downcore, and the isotopic composition of the flux weighted sum of organic carbon remineralization (δ_{total}) would be isotopically different than the organic matter. Isotope discrimination might occur during the fermentation of lower weight organic matter to form acetate and other intermediates, however its signal may not be expressed if most of the organic matter flows through the acetate pathway (Blair and Carter, 1992). An acetate $\delta^{13}\text{C}$ measurement from the sulfate reduction zone of Cape Lookout Bight sediments of -17.6 per mil indicates that the expressed isotope effect is probably less than 2 per mil during the oxidation of acetate (Blair and Carter, 1992). These observations suggest that the isotopic fractionation of the carbon during the formation of methane via CO_2 reduction and acetate dissimilation occurs in the final steps of CH_4 production and little or no fractionation is expressed in the breakdown of higher molecular weight compounds to form low molecular weight compounds such as acetate. This conclusion is in contrast to the less well-constrained speculations about sedimentary processes that would cause intramolecular isotope effects such as bond rupture (Macko, 1992), polymerization, and decarboxylation (Galimov, 1980) and thus alter the isotopic composition of the residual organic matter.

SUMMARY AND CONCLUSIONS

The carbon isotopic signal of the remineralized organic matter in Cape Lookout Bight sediments is -18.9 ± 2.7 per mil based on a mass balance of the remineralized carbon fractions. This estimate is indistinguishable from the calculated $\delta^{13}\text{C}$ signal of the remineralized organic matter determined from vertically uniform POC profiles of -19.2 ± 0.2 per mil. The agreement confirms that the major sources and sinks of carbon and their isotopic signals have been quantified. The comparison of directly measured and calculated CH_4 and ΣCO_2 isotope fluxes suggest that a surficial process is altering the isotopic composition of these species diffusing out of the sediment. Methane oxidation has altered the isotopic compositions of both the ΣCO_2 and CH_4 leaving the sediment, but can account for little of the discrepancy in calculated versus measured $\delta^{13}\text{C}$ values of the ΣCO_2 fluxes.

The isotope mass balance revealed little variation in the isotopic composition of the organic matter being deposited, remineralized, or buried. This is in contrast to numerous recent studies that have focused on organic matter source variations, individual biochemical components and their selective loss or preservation, and also intramolecular isotope effects to explain downcore changes in $\delta^{13}\text{C}$ values of POC (Galimov, 1980; Spiker and Hatcher, 1984; 1987; Benner et al., 1987; Alberts et al., 1988; Hayes et al., 1990; McArthur et al., 1992). The absence of an expressed diagenetic isotope effect in a system with a mixture of organic matter sources suggests that the processes that have been speculated to cause the isotopic variations in sedimentary organic matter profiles may not typically be expressed in the sedimentary

record, and the variations seen may more often be source related (Dean et al., 1986).

A carbon isotope mass balance was achieved by seasonal measurements of the dominant components of the carbon cycle in this system, highlighting the importance of considering seasonality when determining an isotopic signal for a specific environment. This is particularly important in coastal systems where the rates of remineralization processes and the isotopic signals of the various fluxes should vary seasonally.

Fig. 2.1 Cape Lookout Bight particulate organic carbon concentration (A) and $\delta^{13}\text{C}$ values as a function of depth in the seabed. (B) POC profiles are from Chanton et al. (1983); Blair et al. (1987), Blair and Carter (1992) and this study.

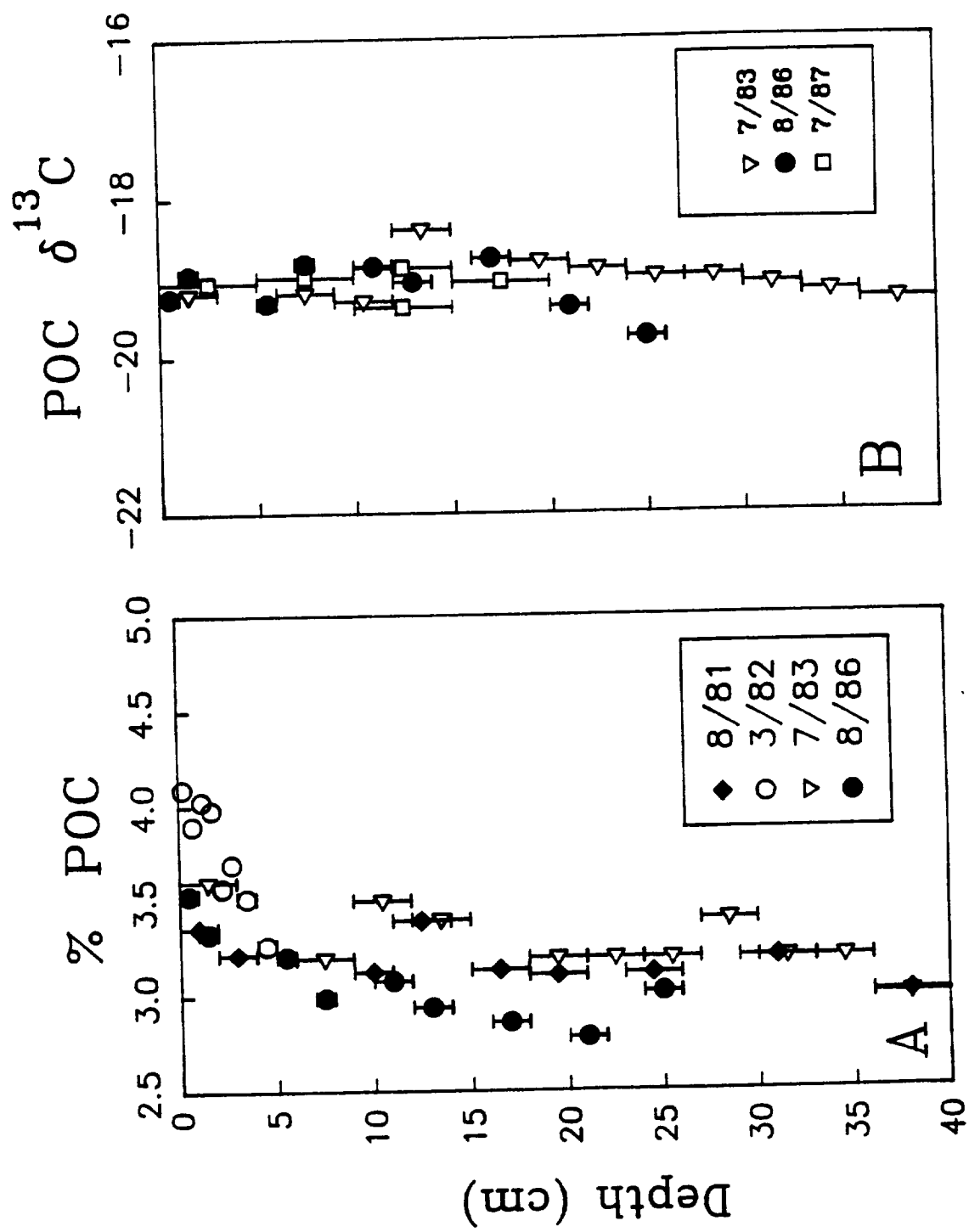
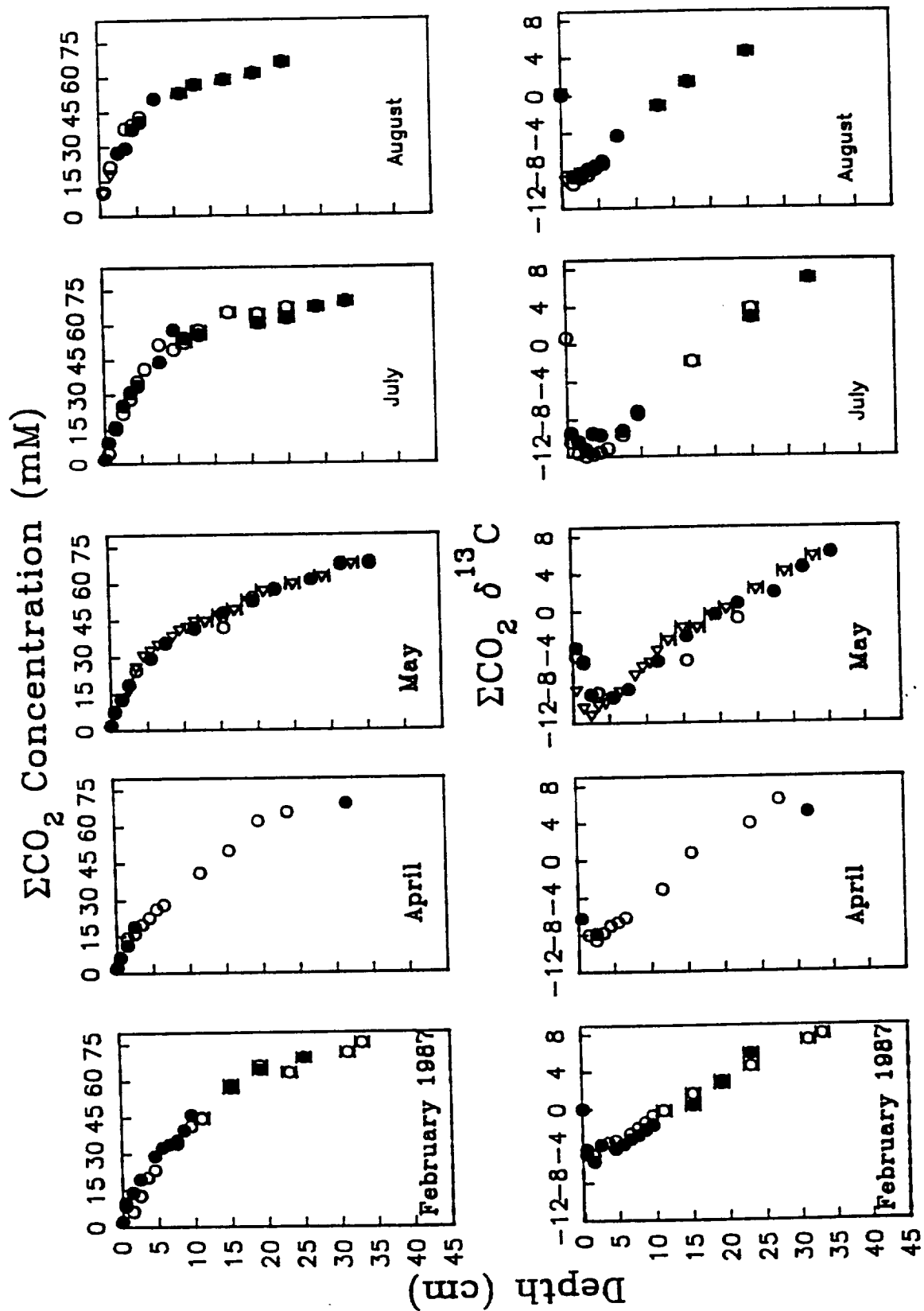


Fig. 2.2 ΣCO_2 concentration and $\delta^{13}\text{C}$ profiles from Cape Lookout Bight. Samples were collected in 1986 except where noted. Individual symbols represent separate cores collected on the same sampling date. The open and filled circles for the May 1986 profiles represent duplicate samples from the same core. Note differences in concentration, depth, and $\delta^{13}\text{C}$ scales for March profiles.



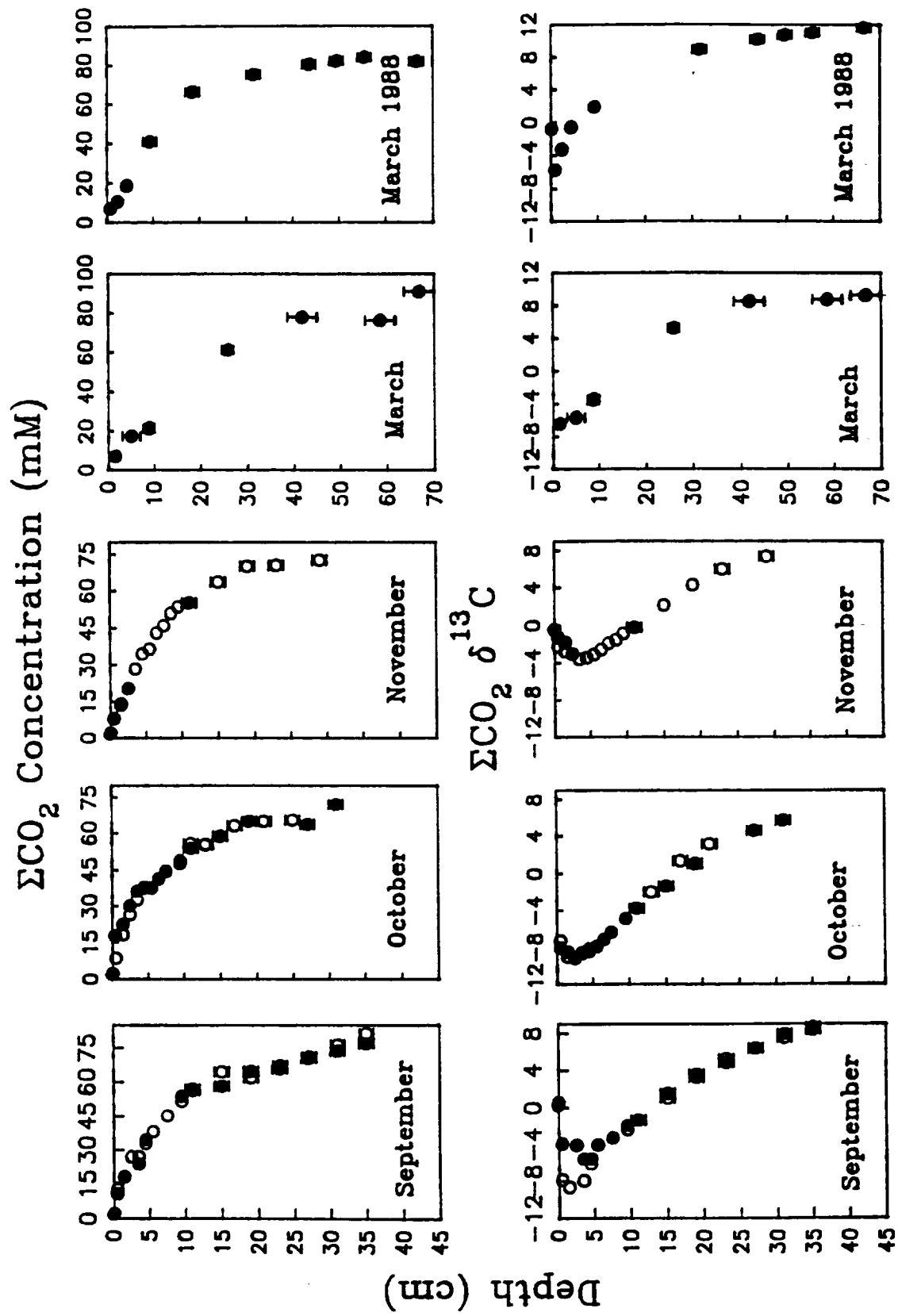
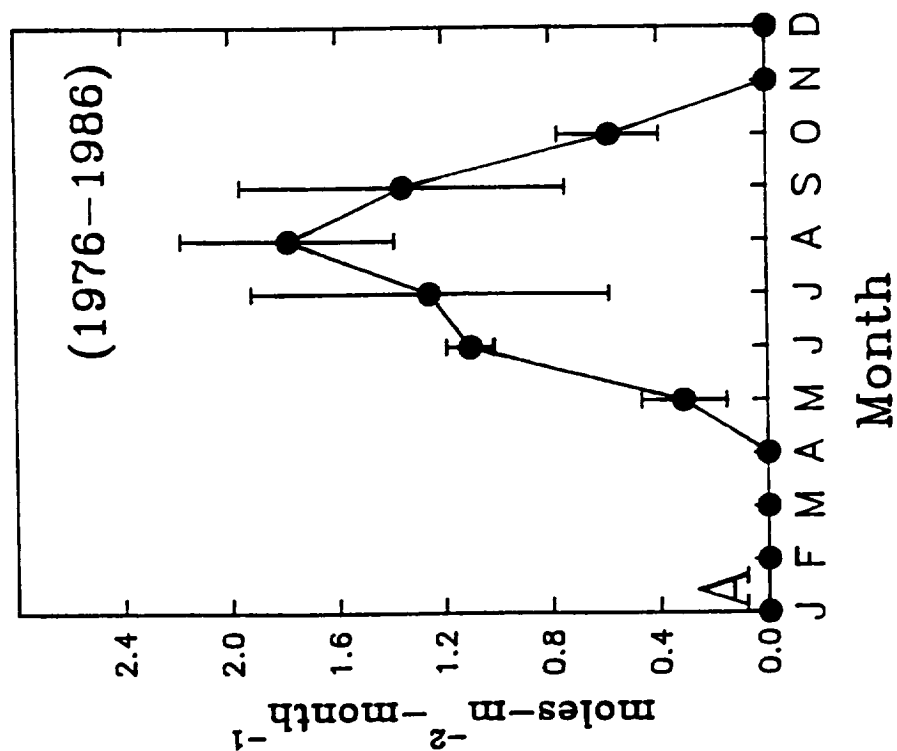


Fig. 2.3

Methane flux and $\delta^{13}\text{C}$ bubble data from Cape Lookout. The ebullitive fluxes from mid October to May are essentially zero. Flux and 1983-1984 $\delta^{13}\text{C}$ bubble data are from Martens et al. (1986). $\delta^{13}\text{C}$ bubble data for 1986 are from this study.

Methane Flux



Methane Bubbles

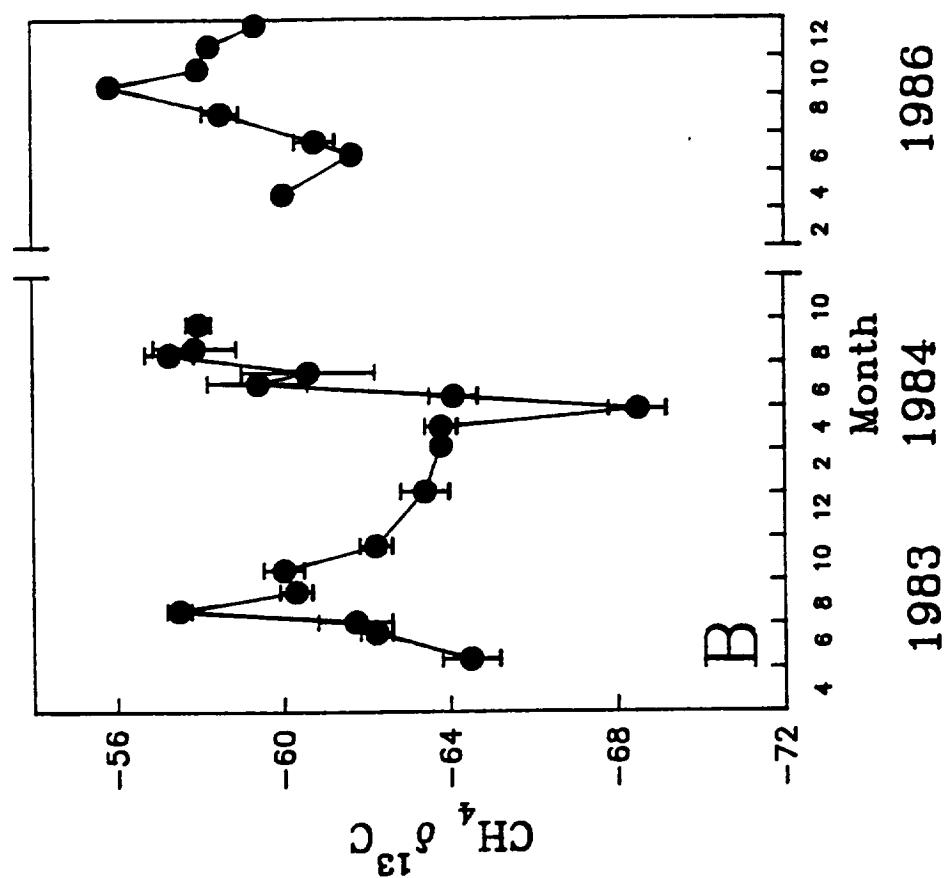


Fig. 2.4 Sedimentary CH₄ $\delta^{13}\text{C}$ profiles from Cape Lookout Bight.

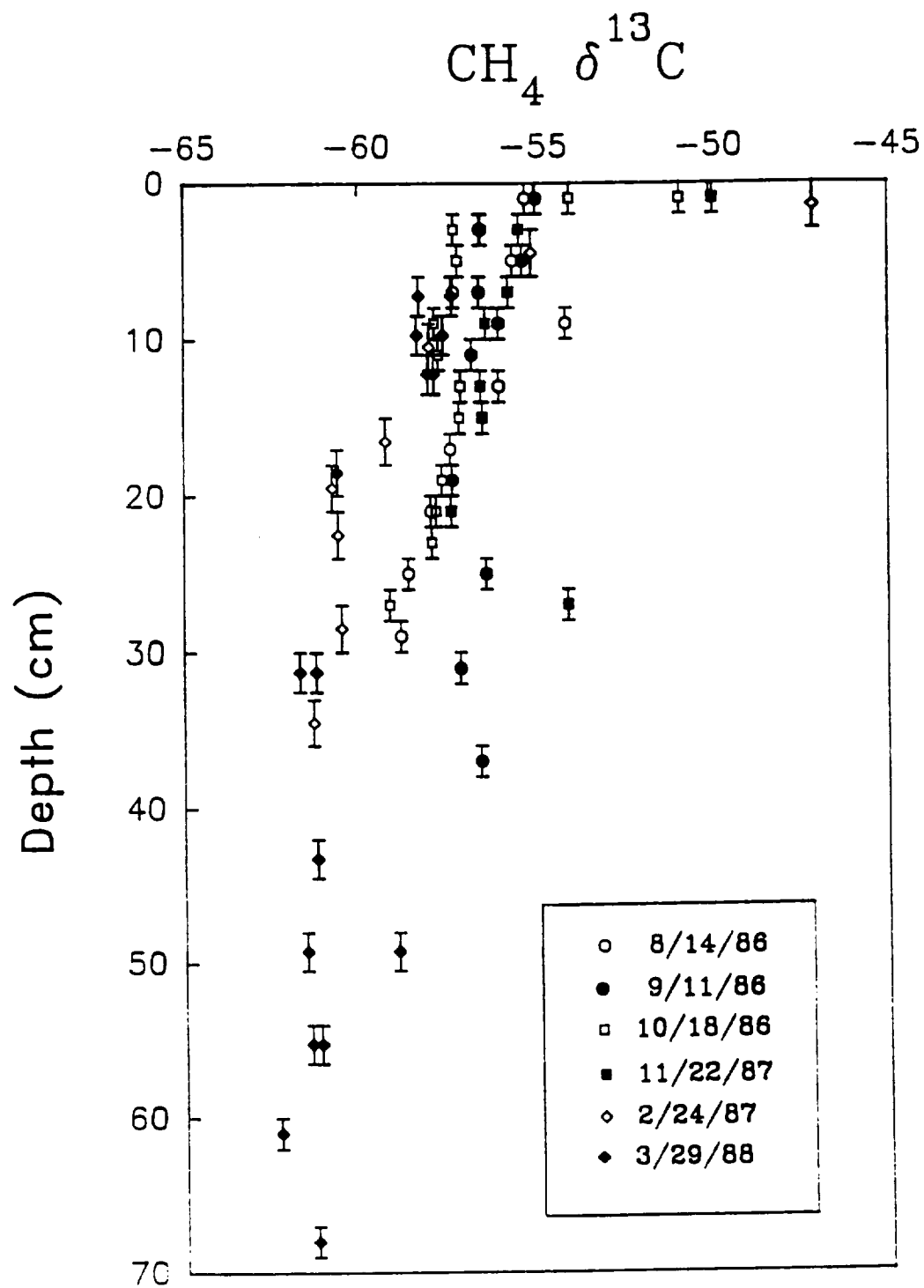


Fig. 2.5 Cape Lookout Bight porewater calcium profiles from 1990-91 (A) and particulate inorganic carbon concentration (PIC) and $\delta^{13}\text{C}$ profiles (B). The dotted line at 5 cm indicates the maximum depth assumed for net dissolution and 5 to 25 cm is considered the zone of precipitation.

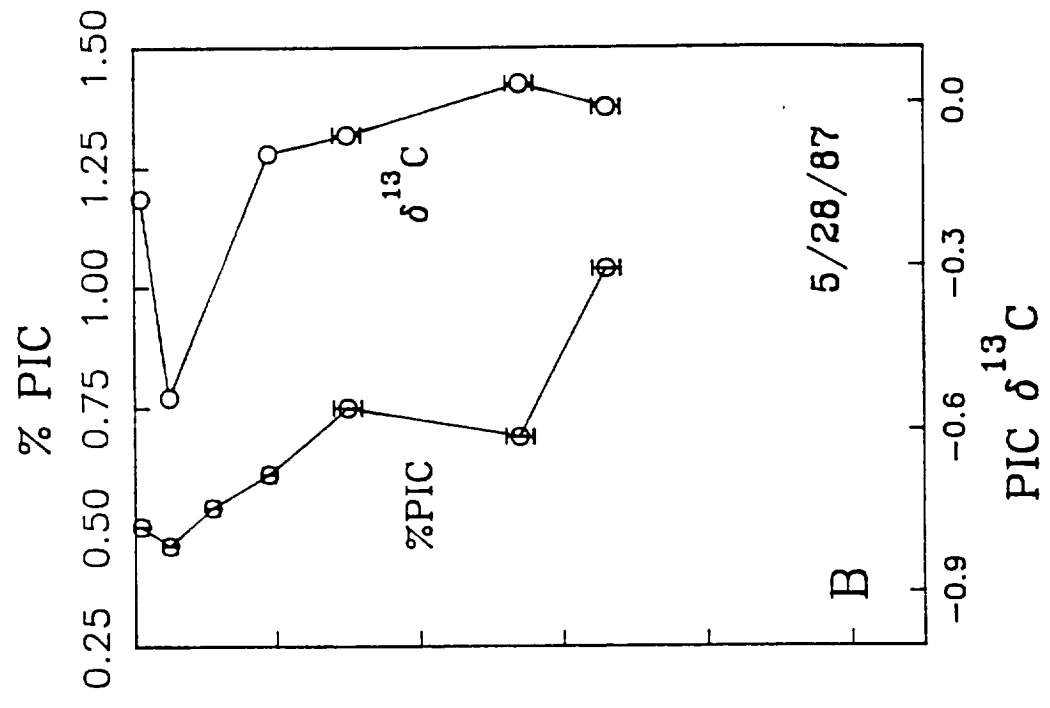
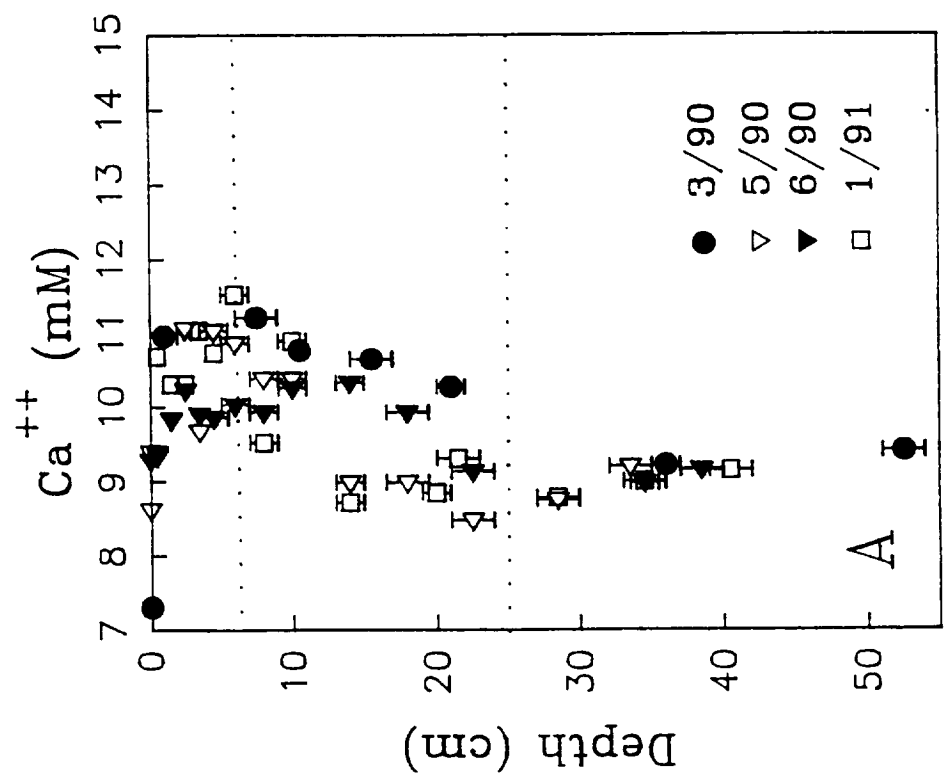


Fig. 2.6 The carbon flow and isotopic composition of the major fluxes at CLB.
The double arrows for methane and CO₂ represent diffusion and bubble ebullition. Carbon fluxes are given in parentheses.

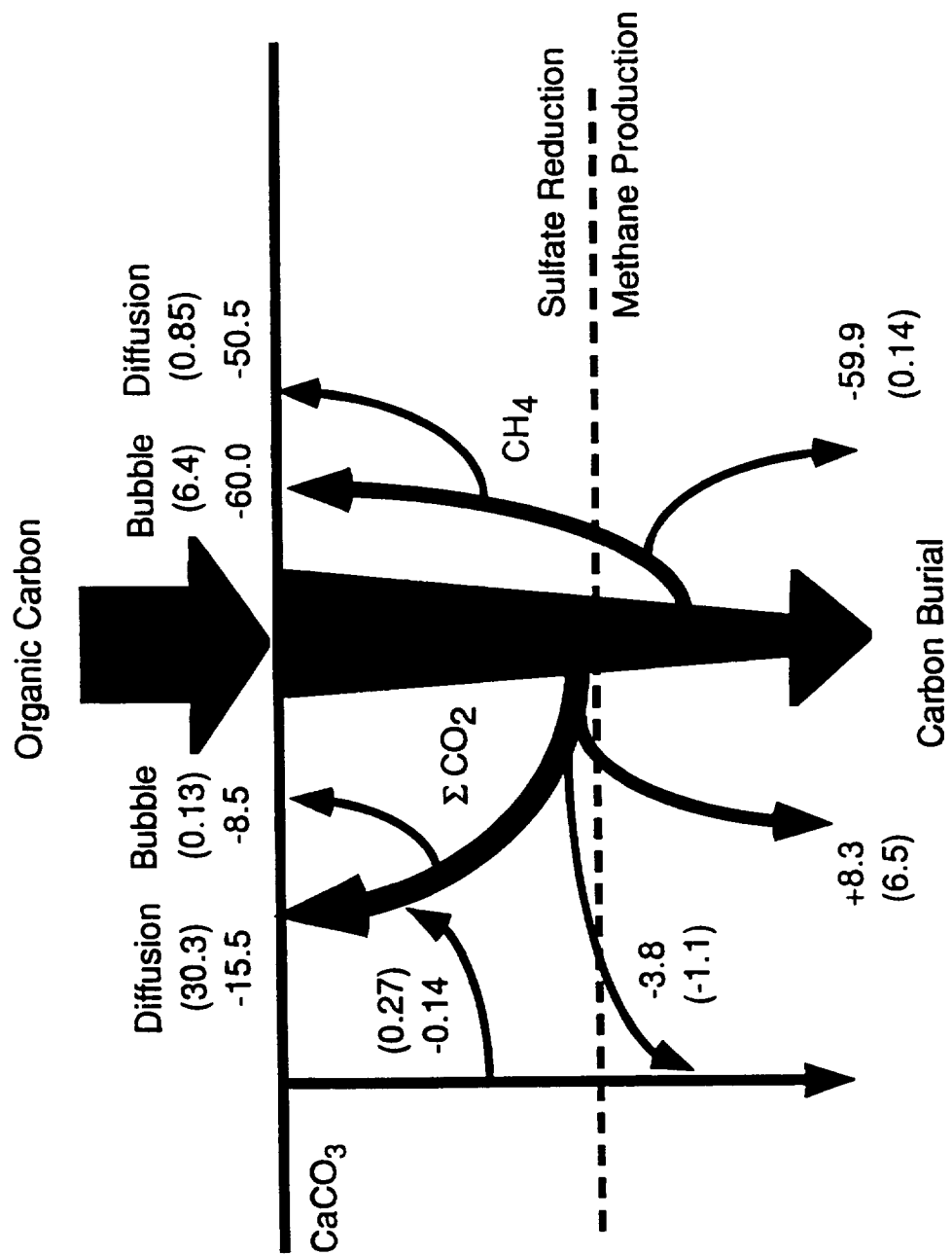


Table 2.1 Fluxes and $\delta^{13}\text{C}$ values of diffusive ΣCO_2 and CH_4

ΣCO_2		Measured		Calculated ¹	
Date	°C	$\text{mmol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$	$\delta^{13}\text{C}$	$\text{mmol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$	$\delta^{13}\text{C}$
4/28/86	17.0	2.20(0.8)	-16.8(2.7)	2.31 ²	-9.7 ²
2/24/87	9.0	1.57	-15.4	1.36	-8.4
3/28/88	15.5	2.54(0.02)	-14.6(2.7)	2.21(0.2)	-8.2(1.4)

CH_4		Measured		Calculated ¹	
Date	°C	$\text{umol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$	$\delta^{13}\text{C}$	$\text{umol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$	$\delta^{13}\text{C}$
3/28/88	15.5	29.2(9.1)	-50.5(0.3)	42.8(7.3) ³	-54.0(0.3)

¹Fluxes were calculated using Eqn. 3. Numbers in parentheses are the range of the average of two chambers. Calculated isotopic signatures are determined from isotopic gradients.

²The April 1986 flux experiment was conducted in-situ. The cores were collected beside rather than directly beneath the chamber for the determination of a calculated flux.

³Methane diffusion coefficient taken from Alperin (1988) and corrected for temperature and porosity.

Table 2.2 Concentration and $\delta^{13}\text{C}$ of ΣCO_2 and individual dissolved inorganic species in flux experiments for March 1988.

ΣCO_2			[mM]				$\delta^{13}\text{C}$			Flux*	
Chamber	Depth	pH	[mM]	$\delta^{13}\text{C}$ ΣCO_2	CO_2	HCO_3^-	$\text{CO}_3^{=}$	CO_2	HCO_3^-	$\text{CO}_3^{=}$	$\delta^{13}\text{C}$ BW to 1cm
P	BW	7.76	2.77	-3.10	0.05	2.63	0.09	-11.8	-2.9	-4.8	-6.8
	0-1cm	7.18	7.28	-5.41	0.48	6.73	0.07	-13.7	-4.8	-6.7	(-6.8)**
Q	BW	7.76	2.87	-3.60	0.05	2.73	0.09	-12.3	-3.4	-5.3	-9.6
	0-1cm	7.18	6.64	-7.03	0.44	6.14	0.06	-15.3	-6.4	-8.4	(-9.7)**

*Flux and isotopic signal of each species determined individually then the following equation was used to solve for $\delta^{13}\text{C}$ ΣCO_2 total flux:

$$\delta^{13}\text{C}_{flux} = \frac{(J_{[\text{CO}_2]} \delta_{[\text{CO}_2]} + J_{[\text{HCO}_3^-]} \delta_{[\text{HCO}_3^-]} + J_{[\text{CO}_3^{=}]})}{J_{[\Sigma\text{CO}_2]}}$$

**Values in parentheses are calculated fluxes based on ΣCO_2 treated as whole species where $(\partial\text{C}/\partial z)$ (Eqn. 3) is based on the ΣCO_2 gradient from bottom water (T_{final}) to 0-1 cm.

Table 2.3 CH₄ Bubble Flux from Martens et al. (1986) and Martens and Chanton (1989).

(moles-m ⁻² -month ⁻¹)							
Month	1976	1977	1978	1985	1986	Average	s.d.
May				0.08	0.54	0.31	0.32
June		0.98		1.23		1.10	0.18
July		0.31		2.21		1.26	1.35
Aug	0.70	1.71	1.57	2.94	2.02	1.79	0.81
Sept	0.46		0.86	2.75		1.36	1.22
Oct	0.71		0.16	0.89		0.59	0.38
Sum (mol-m ⁻² -yr ⁻¹):						6.4	2.1*

*Error was determined as:

$$\sigma = \sqrt{\sum (s.d.)^2}$$

Table 2.4 Carbon isotope mass balance for Cape Lookout, Station A-1.

	moles-m ⁻² -yr ⁻¹	δ ¹³ C
CH₄		
Buried	0.14(0.02)	-59.9(1.9)
Bubble	6.4(2.1)	-60.0(1.2)
Diffusive	0.85(0.8)	-50.5(0.3)
ΣCO₂		
Buried	6.5(0.5)	+8.3(1.5)
Bubble	0.13(0.05)	-8.5(1.4)
Diffusive	30.3(4.8)	-15.5(1.2)
J_{total}	44.3(12.6)	-19.2(2.7)¹
PIC		
Dissolved	0.27(0.4)	-0.14(0.2)
Precipitated	-1.1(0.3)	-3.8(3.8)
J_{remin}²	45.13(12.6)	-18.9(2.7)

¹The estimated δ¹³C of the flux (J_{total}) was determined using the following equation:

$$\delta^{13}C(J_{total}) = \frac{\sum [(\delta J_i) (J_i)]}{\sum (J_i)}$$

where i = the diffusive, ebullitive and burial fluxes of CH₄ and ΣCO₂.

²Calculated using Eqn. 5.

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